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Spatial and Temporal Patterns of Acid Precipitation and Their Interpretation

Analytical Sciences, Inc.
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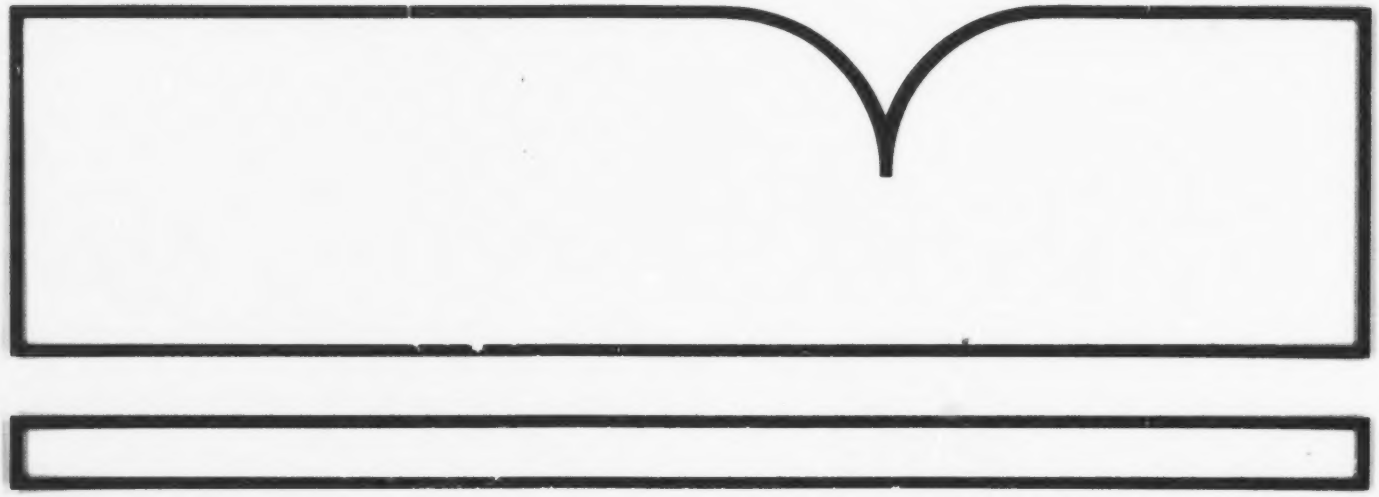

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ABSTRACT

Using data compiled from seven nationwide precipitation chemistry networks in the U.S. and Canada, the spatial distribution of hydrogen, sulfate, and nitrate ions in North America is discussed. Geographic patterns of concentration and deposition are characterized using isopleth maps which are presented and interpreted for the years 1980-1983. The maps were developed using a geostatistical technique known as "kriging". This method allows for the estimation of confidence limits on interpolated values. Using these limits, the significance of temporal changes in spatial patterns of deposition and concentration is assessed. The data discussed in the presentation were compiled and initially summarized by Battelle Northwest Laboratories in the operation of the Environmental Protection Agency's Acid Deposition System (ADS).

INTRODUCTION

Although there is widespread concern over the effects of acid precipitation, we have very little information about its past and present distribution over North America. For a few monitoring sites there is a long record of pH measurements, but in general we have only recently obtained enough data to regionally characterize acid precipitation levels. With the present monitoring network density one is now able to quantify concentration and deposition of sulfate, nitrate, and hydrogen ion in precipitation. In this paper, we investigate the spatial distribution of these constituents of acid precipitation in 1980-1983, the period in which a relatively large number of stations have collected samples and made chemical measurements. Our analysis provides a characterization of the geographic pattern of acid precipitation, and assesses whether there is evidence of significant changes in patterns over that time period.

DATA

Data in this report were gathered and summarized by the Acid Deposition System (ADS), an acid rain data bank operated by Pacific Northwest Laboratories for the U.S. Environmental Protection Agency (Olsen and Watson, 1984). The report includes data from:

- NADP (National Atmospheric Deposition Program)
- MAP3S/PCN (the MAP3S Precipitation Chemistry Network)
- CANSAP (Canadian Network for Sampling Precipitation)

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- APN (The Canadian Air and Precipitation Monitoring Network)
- EPRI/SURE (EPRI Sulfate Regional Experiment Precipitation Chemistry Monitoring Program)
- UAPSP (Utility Acid Precipitation Study Program)
- APIOS (Acid Precipitation in Ontario Study)

A brief summary of the deposition networks is given in Table 1. Each network has its own program for data quality assurance. In addition, ADS screens the data for reasonableness and completeness. We also checked the data a third time and removed a few outliers.

TABLE 1. DESCRIPTION OF MONITORING NETWORKS

Network	Geographical Area	Number of Sites As of 1982	Sampling Period
NADP	National Coverage of United States	117	Weekly samples collected each Tuesday
MAP3S/PCN	Eastern United States	9	Event samples
CANSAP	National Coverage of Canada	62	Monthly samples collected on last day of month
APN	Eastern Canada	9	Daily samples
APIOS C	Ontario Province	36	Monthly samples
APIOS D	Ontario Province	16	Daily samples
EPRI/SURE	Eastern United States	18	Event samples
UAPSP	Eastern and Central United States	19	Daily samples

In this analysis only annual data are used. Concentrations are given as volume-weighted averages while deposition represents a total over the year. For each site, decisions had to be made on whether or not there were enough individual samples to constitute a valid annual average. Three sampling representativeness criteria were used to determine from which stations annual averages would be used. They were:

(1) Percent Precipitation Coverage Length (PPCL) the percent of the days in the year for which valid precipitation measurements are available.

(2) Percent Total Precipitation (PTP) - the percent of the total precipitation that occurred during valid sampling (i.e., when good samples were taken) to the total measured precipitation. This figure would be low, for example, if there were significant rainfall while the samplers were inoperative.

(3) Percent Valid Sampling Length (VSL) - the percent of the year during which valid sampling could occur whether it rained or not. This is 100 minus the percent of the time the collector was known to be inoperative.

In addition, a fourth criterion was used to judge the quality of the sample. It is Percent Collection Efficiency (PCE). PCE is the ratio expressed as a percent of the total sample volume for the year (expressed as a depth) to the total yearly depth measured in the recording rain gage colocated with the collector. It is a measure of the quality of the site, the maintenance of the collector (and gage) and an indication of unusually high winds or snowfall which affect collector performance. For this study the criteria used to accept annual averages from a station are:

PPCL > 80% PTP > 65% VSL > 65% PCE 65% to 125%

These are rather loose criteria which were chosen to maximize the number of stations in order to best define the patterns to be analyzed. It was felt that a few possibly misleading values would not make a significant change in the results. If one were interested in detailed analysis of individual stations, more stringent selection criteria should be used.

These screening criteria were applied to annual data from eastern North America (east of 94 degrees west longitude) resulting in the following numbers of sites available for analysis.

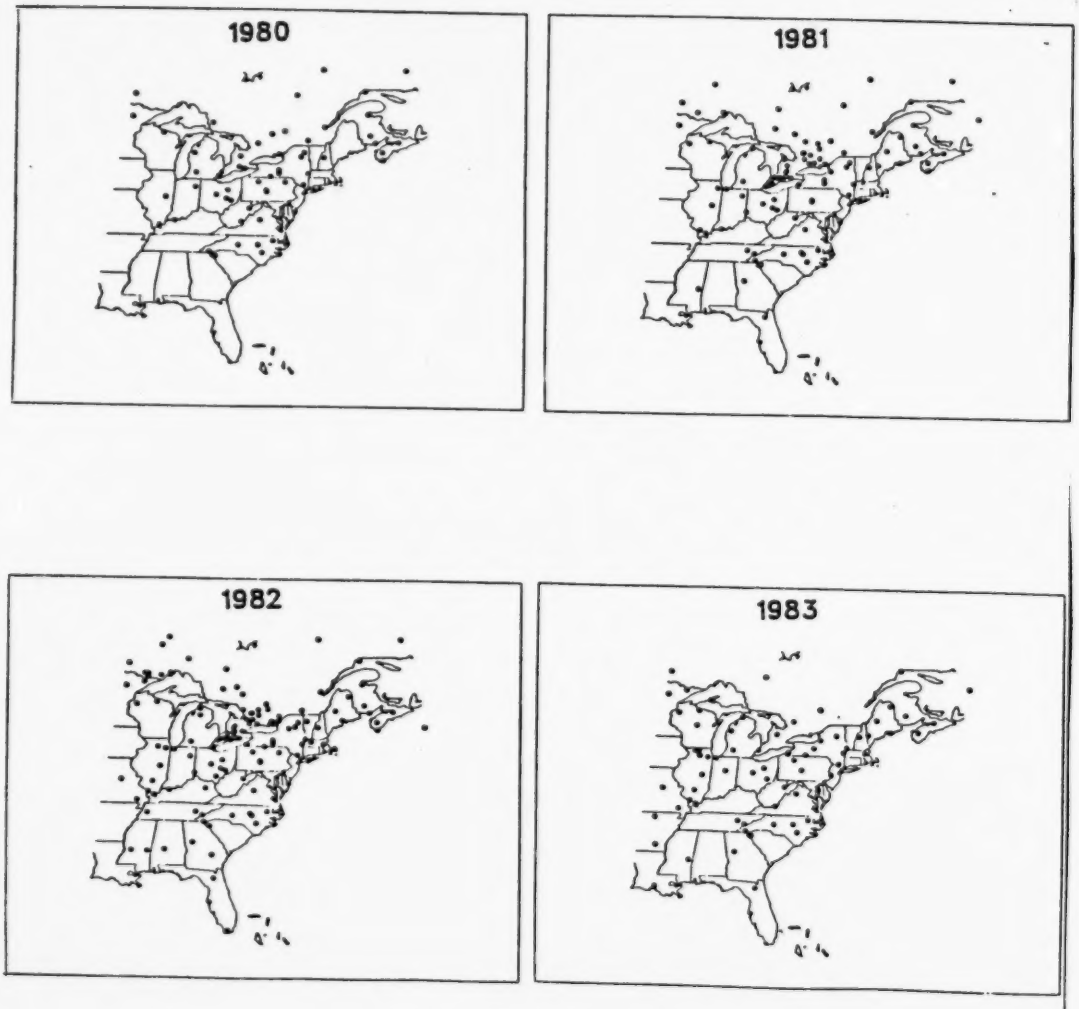
Year	1980	1981	1982	1983
Sites	62	99	133	67

The site locations are illustrated in Figure 1. The relatively small number of monitoring stations depicted in 1983 is due to unavailability of data at this time rather than a reduction in monitoring activity. There are now more than 250 monitoring sites in North America. These maps clearly show the increases in monitoring activity since 1980, particularly that occurring in southern Ontario. They also demonstrate that the monitoring sites available for spatial analysis are quite irregularly spaced, with heavy sampling densities in some areas, e.g. eastern Ohio and eastern Nova Scotia, and pockets of low density as seen in central Illinois, Maine, and Quebec. The differential in sampling density has an inpact on the geographical characterization and interpretation of the data from these sites. Clearly we should have greater confidence in summary measures for areas represented by large numbers of sites than for those with sparse monitoring site coverage.

METHODS

The investigation of spatial and temporal trends in acid precipitation required a visual means to represent geographic patterns. Isopleth maps were used to provide characterizations of concentration and wet deposition of sulfate, nitrate, and hydrogen ion over eastern North America for each of the years 1980-1983. These maps are a powerful way to portray the general spatial features of the data, but should be used judiciously. It

FIGURE 1
MONITORING SITES
EASTERN NORTH AMERICA
1980 - 1983



should be understood that there is uncertainity (error) in the location of an isopleth due to the random variation in the data on which it is based. Just as a sample mean imperfectly estimates the population mean, the isopleth imperfectly represents the true response surface associated with a spatial variable. Unfortunately, most mapping techniques for producing isopleths are incapable of reflecting the imprecision in the location of the isopleths due to their reliance on interpolation and smoothing algorithms which fail to quantify and utilize measures of data variability.

In order to redress these problems, a method known as "kriging" was used to provide a representation of the geographic pattern of acid precipitation. Unlike most other techniques, it uses the variability in the data to determine the weighting scheme for estimating unknown values. It also quantifies interpolation error. Kriging is actually a family of "geostatistical" estimation procedures. It was named for a South African mining engineer, D.H. Krige, and has been used primarily in the mining industry. However, this methodology is becoming increasingly popular in other fields (see Barnes, 1980, for descriptions). It has been found to be a particularly useful tool for analyzing spatial trends in acid precipitation data (Finkelstein and Seilkop, 1981; Finkelstein, 1984; Bilonick, 1983; Eynon and Switzer, 1982).

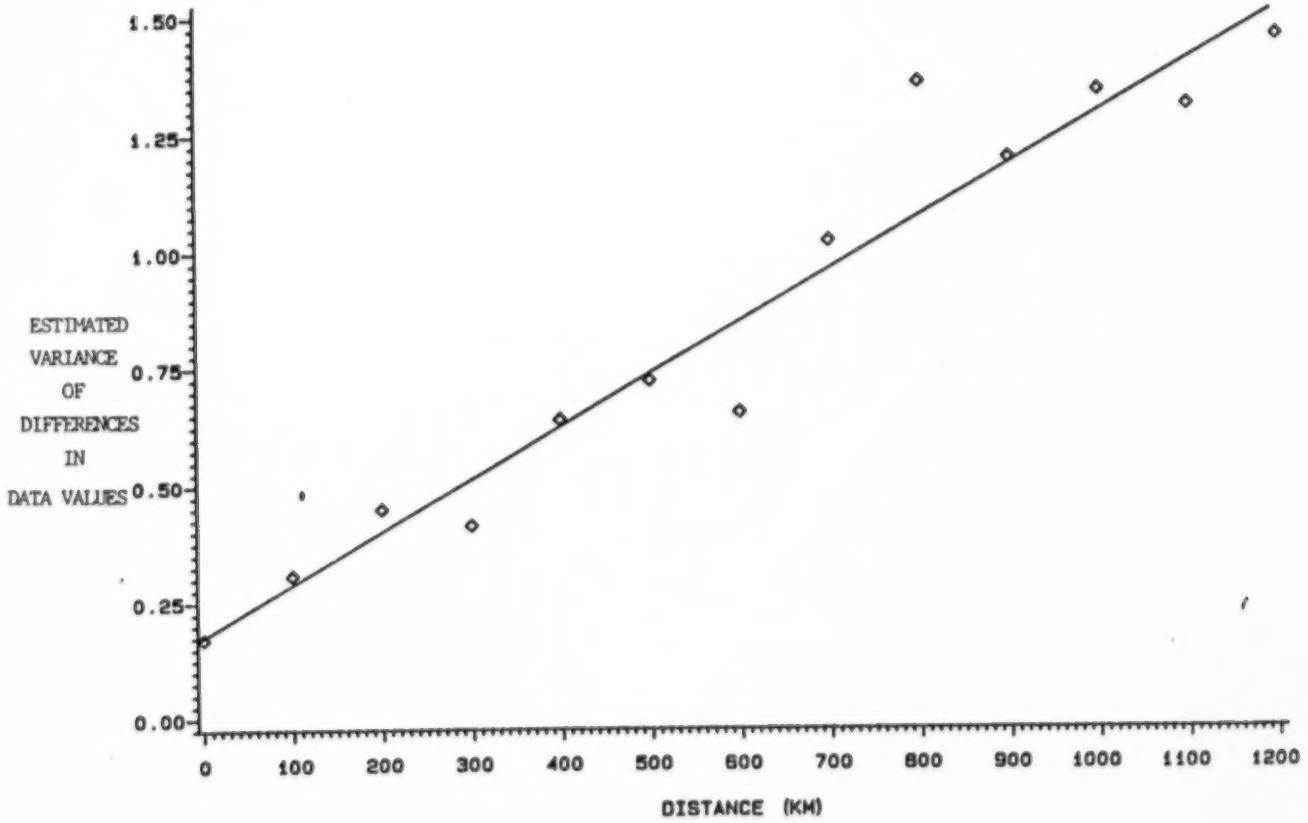
All kriging techniques rely on a model of the spatially- and/or temporally-related covariance structure of the data under analysis. In simple kriging, which will be used in this paper, spatial variability is modeled by the variogram, a function which relates the variance of station-to-station differences to the distance between stations. A typical variogram is displayed in Figure 2. Its positive slope reflects decreasing correlation between data as the distance between monitoring sites increases. The Gamma intercept can be interpreted as the underlying error in the measurement process. Several general models for variograms have been proposed (see Delhomme, 1979 for details). In this example, a straight line would be used.

Several forms of kriging (e.g. universal, generalized covariance) have been developed to remove the effect of data trends on the estimation of the spatial covariance structure. Simple kriging, however, views all variation as random. Consequently, a variogram which contains some systematic (trend) components can lead to inflated estimates of interpolation error. However, the estimation bias is not serious under moderate spatial trends (Journel and Huijbregts, 1978; Seilkop, 1985). In an effort to understand the extent and effect of trends on variogram estimation, overall and directional (N-S, E-W, NE-SW, NW-SE) variograms were estimated for deposition and concentration of sulfate, nitrate, and hydrogen ion. In this analysis, for simplicity, the overall nondirection variograms were employed in the calculation of all kriging interpolation weights and variances. In all cases straight lines were found to be adequate models for variograms at distances less than 1200 km.

In order to characterize acid precipitation, the available monitoring site data were used to obtain kriging estimates of values at 270 regularly spaced grid points across eastern North America. These estimated values define a relatively smooth surface which retains the primary features of the spatial data. The variability in the location of isopleths was depicted with one standard deviation "confidence isopleths" which are derived using the kriging interpolation error variance estimates (see Finkeltein, 1984; Seilkop, 1985). Upper and lower confidence isopleths provide an envelope of uncertainty on a given

FIGURE 2

TYPICAL VARIOGRAM



isopleth. If areas bounded by these confidence isopleths fail to overlap across years, there is good evidence for a change in the spatial pattern of the variable being analyzed.

RESULTS

Isopleth maps developed using kriging are presented in Figures 3-5 for sulfate concentration and deposition, nitrate concentration and deposition, and hydrogen ion concentration and deposition, respectively. Each figure contains maps for the years 1980-1983. A few observations are obvious from the data. The patterns for all variables are reasonably well-defined. That is, they each form one major well-defined pattern without large discontinuities or irregularities. There are enough data to say that there is a clear central maximum area in each map with decreasing values around it. Thus, the existing sources and weather patterns do produce a definable area of maximum wet deposition.

Comparing various species, it can be seen that the patterns for SO2, NO3, and H concentration and deposition are very similar for each of the four years. In almost all cases the maximum area is found between southern Ontario, Lake Erie, and northern Ohio to western New York. The shape of the patterns is also quite similar across species, and can be generally described as ellipsoidal, with the major axis running WSW to ENE. Sulfate and hydrogen differ from this pattern somewhat in 1982 as their major axis has more of a North-South orientation. Nitrate does not show this change.

Areas of maximum concentration and deposition seem to remain constant in 1980 and 1981. However, in 1982 there is some evidence of a decrease in the size of the areas with the highest concentrations. This decrease appears to continue through 1983, although a trend is somewhat questionable due to the relative paucity of data in 1983, discussed above. The lack of data from southern Ontario, the area with the highest levels, makes it particularly difficult to assess the apparent 1983 decrease.

The inconsistent sampling density across years, as well as the inherent variability in the estimated isopleths cloud our ability to make definitive statements regarding temporal trends in these data. An example of the effect of increased sampling density on our confidence in individual estimates of constituents of acid precipitation is shown in Figure 6. These maps depict the variances associated with estimated values in 1980 and 1982. The effect of the doubled sampling density for this period is clearly evident. The large increase in sampling activity in southern Ontario and the addition of sites in the northern U.S. reduce the estimation variance in the area of maximum sulfate deposition by approximately 50%.

The size of the estimation variance for individual values is also quite striking. In a large part of the area of maximum deposition, the coefficient of variation is approximately 20% in 1982 and 30% in 1980. Clearly isopleths derived from such variable estimates should be viewed with caution. As an example, consider the 3.0 mg/l sulfate concentration isopleths shown in Figure 7a. The solid lines are the estimated isopleths and the dashed lines represent the one standard deviation upper and lower "confidence" isopleths. An interpretation of the area bounded by the confidence isopleths is that approximately 70% of the isopleths resulting from a similar, but different configuration of sampling sites would result in a 3.0 isopleth within this region. With 1982 and 1980 there is an overlap of

FIGURE 3
SULFATE CONCENTRATION AND DEPOSITION
1980 - 1983

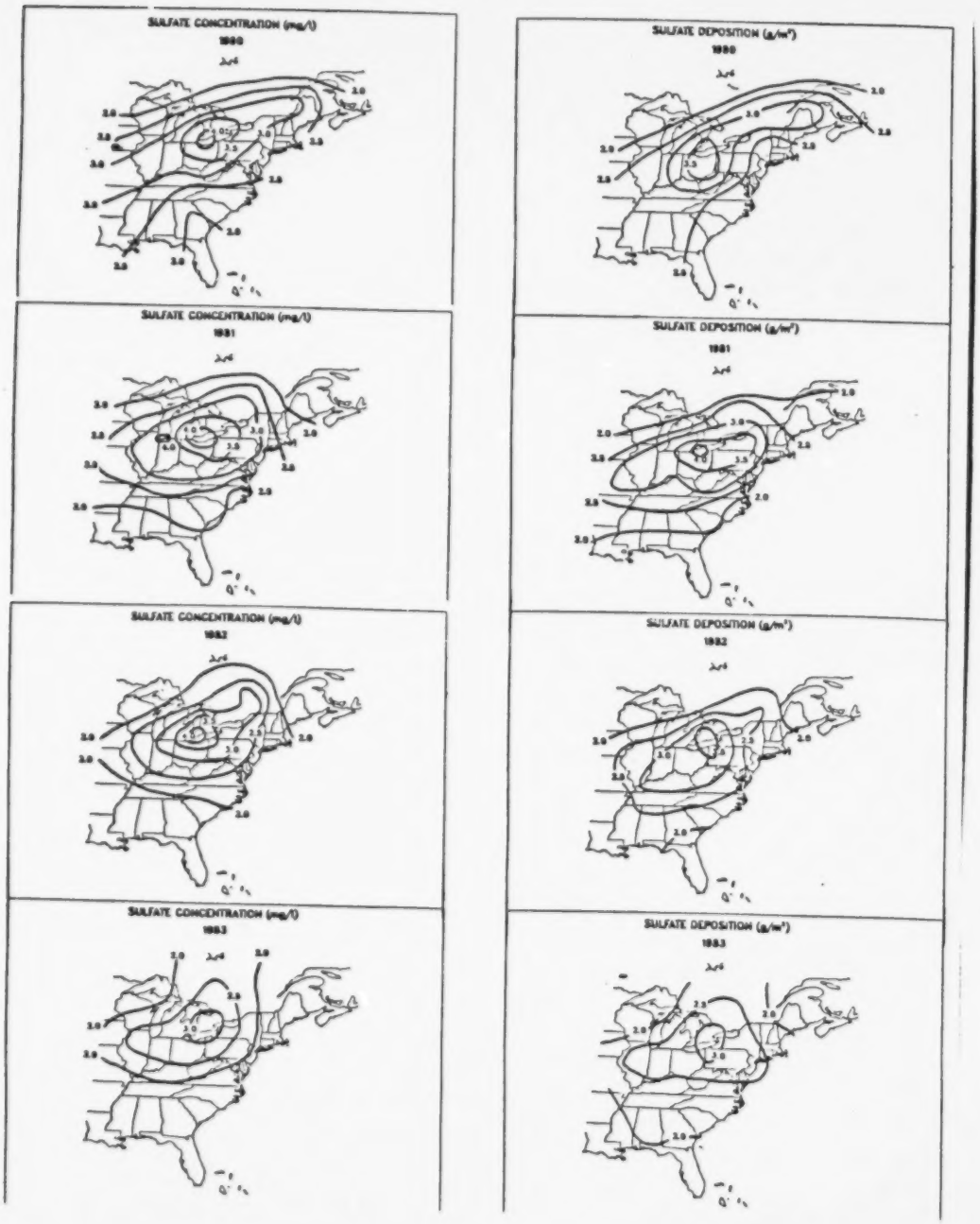


FIGURE 4

NITRATE CONCENTRATION AND DEPOSITION

1980 - 1983

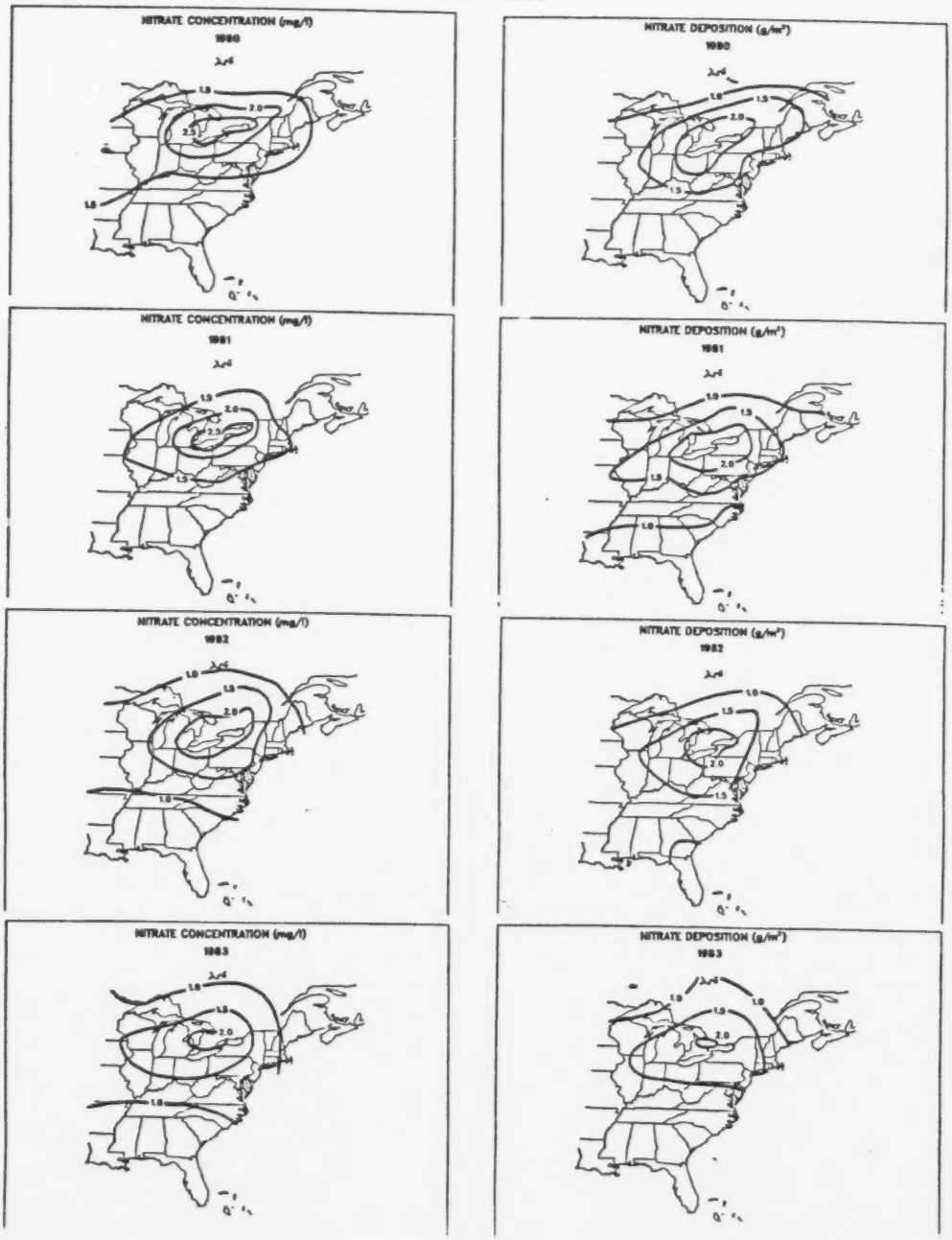


FIGURE 5

HYDROGEN ION CONCENTRATION AND DEPOSITION

1980 - 1983

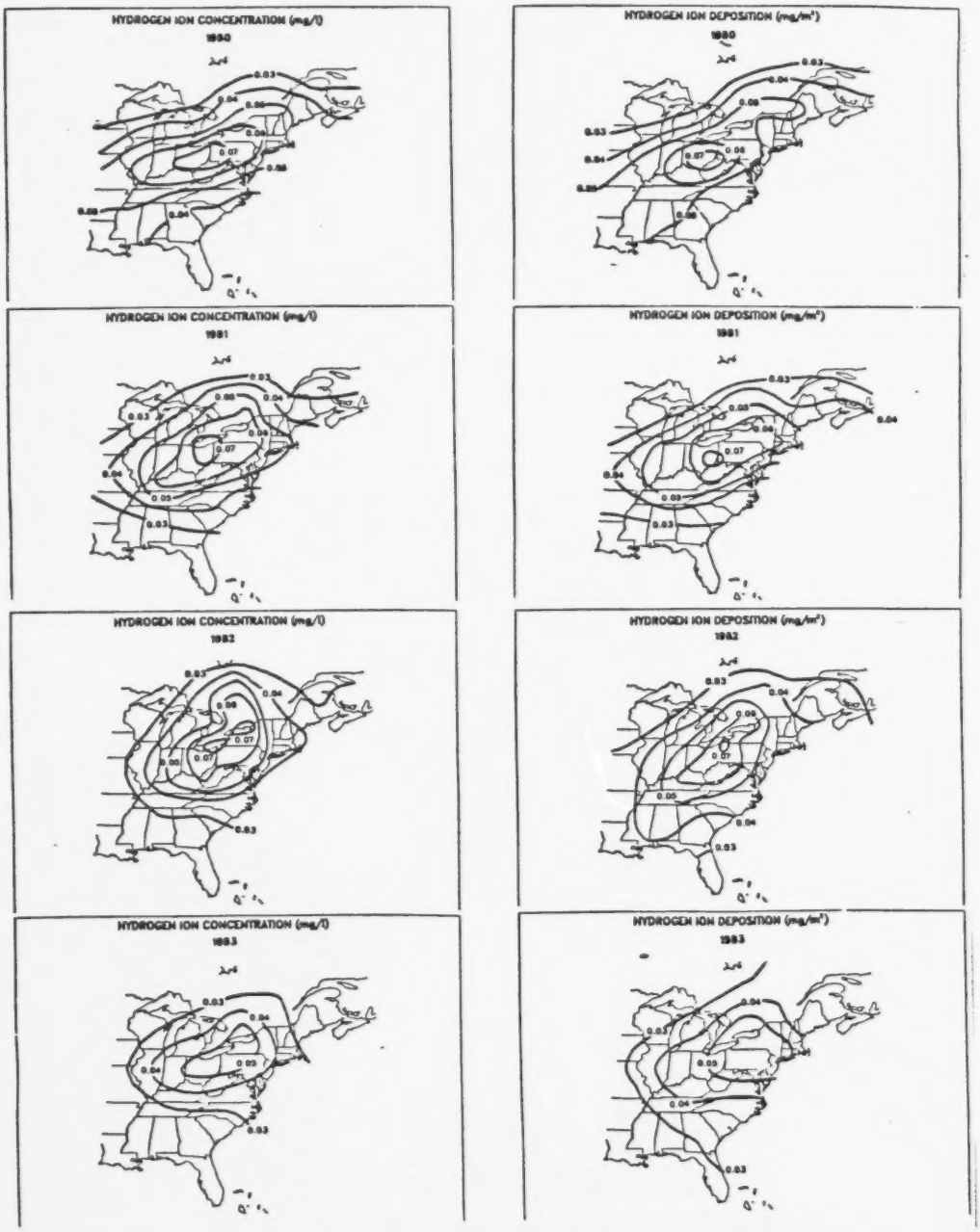


FIGURE 6

SULFATE CONCENTRATION (mg/l)

ISOPLETHS OF ESTIMATION VARIANCE

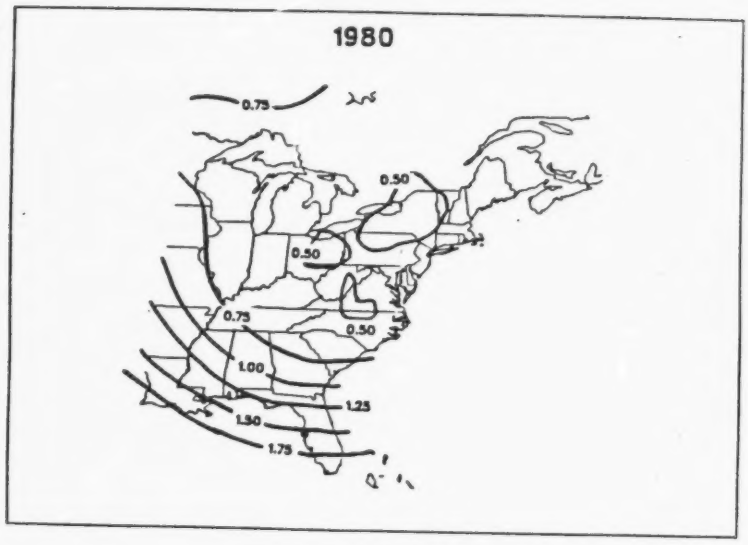
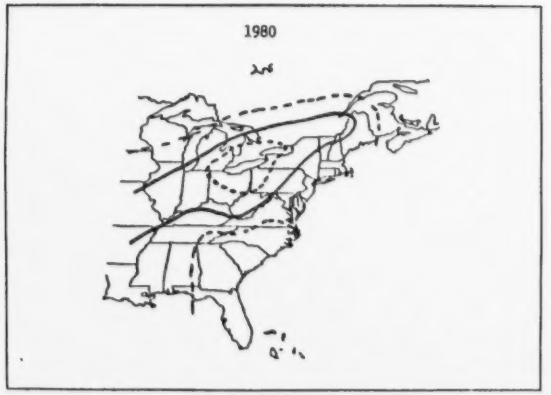


FIGURE 7A

SULFATE CONCENTRATION
3.0 mg/l ISOPLETH AND
UPPER AND LOWER CONFIDENCE ISOPLETHS



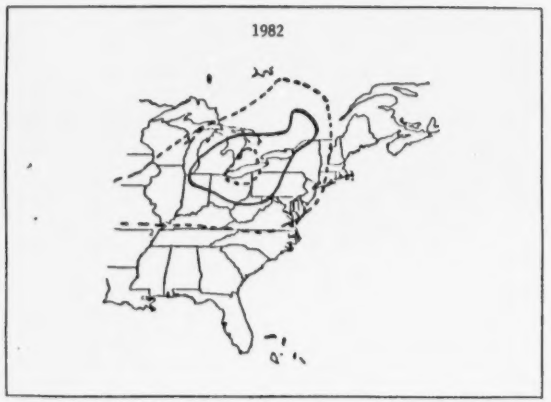


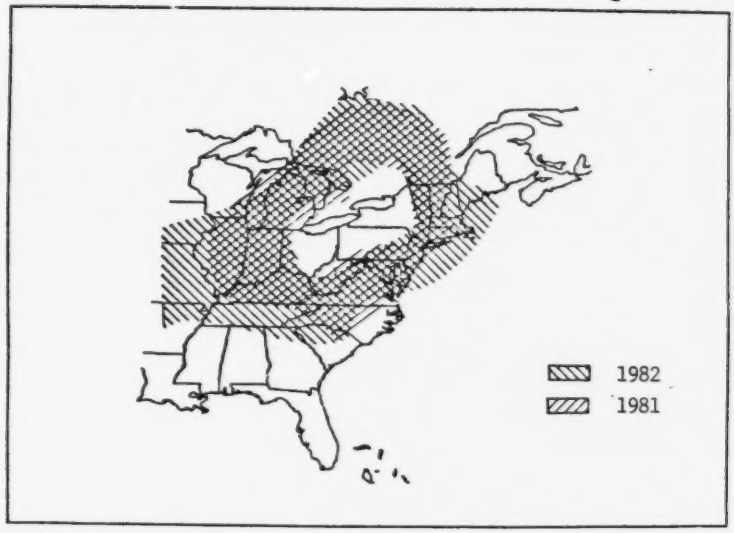
FIGURE 7B

SULFATE CONCENTRATION
4.0 AND 4.5 mg/l
UPPER CONFIDENCE ISOPLETHS

FIGURE 8

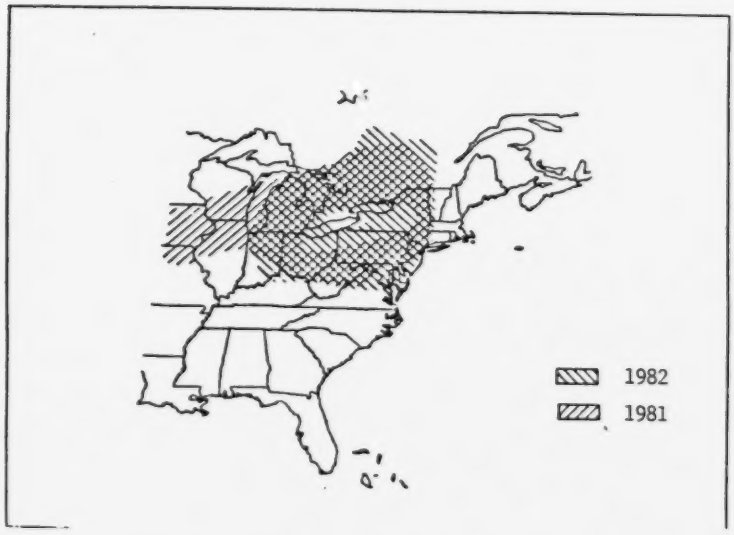
HYDROGEN ION CONCENTRATION

0.05 mg/l CONFIDENCE REGIONS



NITRATE CONCENTRATION

2.0 mg/l CONFIDENCE REGIONS



regions which imples little evidence of a change in this isopleth over time. The similarity in the location and magnitude of the peak concentration is also shown in Figure 7b where the 4 and 4.5 upper confidence isopleths for the two years are nearly identical.

Analyses as used above, which recognizes data variability, was carried out for concentration and deposition of sulfate, nitrate, and hydrogen ion. Figure 8 shows two examples of confidence regions in which shifts in pattern from 1981 to 1982 were suspected from the isopleth maps in Figures 4-6. The overlap in the regions for both nitrate and hydrogen ion concentration suggest that observed changes in pattern are not systematic and should be attributed to the random variation. Other similar analyses of the remaining data gave little evidence to indicate geographic shifts in pattern or changes in magnitude over time.

SUMMARY AND CONCLUSION

The analysis has shown geographic patterns of the distribution of constituents of acid precipitation to be well-defined and consistent for the years 1980-1983. Sulfate, nitrate, and hydrogen ion concentration and deposition were similar in each of these years, with maximum levels found between southern Ontario, Lake Erie, and northern Ohio to New York. There was little evidence of a temporal change in the levels or patterns of acid precipitation over the short period under examination. The high degree of variation observed in the acid precipitation data analyzed here demonstrates the need to carefully interpret spatial characterizations. It also points out the need for increased monitoring efforts and the use of statistical tools such as kriging which equip us to assess changes and trends which may occur over time.

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